U.S. EPA TECHNICAL SUPPORT PROJECT
TECHNICAL SESSION MINUTES

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U.S. EPA TECHNICAL SUPPORT PROJECT CO-CHAIRS

Engineering Forum:
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Meghan Cassidy, Region 1 • Paul Leonard, Region 3
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TABLE OF CONTENTS

PLENARY SESSION

Welcome Address

Opening comments were provided by Max Dodson, Deputy Regional Administrator of Region 8, Warren Bergholz, INEEL, Renee Wynn, FFRRO, Gareth Pearson, NERL, and Larry Reed, OERR.

Dodson welcomed Forum members to Salt Lake City and Region 8. He said the Region is home to several large, complex sites, such as Rocky Mountain Arsenal and Rocky Flats, which are located near Denver. The current estimate to clean up Rocky Flats is $4 billion, but that estimate assumes the Waste Isolation Pilot Project (WIPP) in New Mexico will be approved and start accepting radioactive waste. Without this disposal option, Rocky Flats will not be remediated. He cited several other complex and difficult sites, such as the Air Force Space Command facility in Cheyenne, Wyoming, where the Air Force used a cap on a RCRA Subtitle C facility.

In addition to the technical issues, communication issues also must be addressed. Dodson said EPA needs to do a better job of communicating with the public and explaining the proposed remedies. He acknowledged that it is a “big job” convincing the public EPA is “doing the right thing.” He suggested three approaches for gaining community acceptance: becoming involved early in the process; being honest and open with the public; and forming a collaborative relationship with the community.

Dodson also explained the importance of responding to emergencies and provided two examples: the Alberston train wreck where a significant chlorine cloud was released; and the Grand Forks floods. The lesson from both of these events was the need to provide a timely response and to access technical information quickly. He said an information clearinghouse is needed to allow emergency responders to obtain both technical and anecdotal information quickly.

The TSP Forums can assist with these issues, particularly those of a technical nature. Dodson added that the Agency needs to support the Forums and promote the development of technical knowledge and skill. Relying on good science and technology is a better approach than “seat of the pants” policy making. He added the Forums also provide other valuable services including: preparing issue papers; providing comments on technical issues and policy; participating on workgroups; and disseminating information about treatment technologies.

Bergholz said he views the Forum meeting as an opportunity to share information, to learn from EPA’s experiences, and to identify opportunities for future collaborative efforts. He described INEEL and its mission, which has been primarily focused on nuclear research. The laboratory was established in 1949 as the national nuclear reactor testing facility. Its primary function was the testing of nuclear energy. In 1974, the mission of the laboratory changed and the facility was re-named the Idaho National Engineering Laboratory. Now, the laboratory mission has been expanded to include cleaning up the legacy of the cold war, both at the facility as well as Rocky Flats. Recently, the name was changed to Idaho National Engineering and Environmental Laboratory to reflect this new mission. The laboratory wants to leverage resources to develop better, more efficient technologies for cleaning up the environment.

Bergholz said INEEL is an engineering laboratory with broad expertise in various fields. Because the facility itself is a Superfund site, INEEL can test innovative technologies on its own property. It has established a test bed for that purpose on INEEL property. In addition, as a Federal laboratory, it can transfer federally-developed technologies to private industry. INEEL can help EPA in several ways, including: assisting the Technical Support Project and the Superfund Science Division; providing technical support to EPA’s ORD laboratories;

participating on the Remediation Technologies Development Forum; coordinating with EPA on INEEL's Superfund cleanup activities; and working with EPA and private industry to test innovative treatment technologies.

Wynn said Forum meetings present good opportunities to network, share information, and form partnerships. She said it is good to hear the different perspectives of the various EPA Regional and Program Offices and other Federal agencies. Rather than the typical "mind-to-mind" transfer of information, these meetings allow extensive information sharing among a wide group of people. This information can then be shared with other colleagues when everybody returns to their office.

This information sharing is particularly important for Federal facilities. Last year, 91 RODs were signed at Federal facilities and this year 100 are expected to be signed. There is an opportunity for creative solutions at these facilities and this meeting serves as a vehicle for learning about applicable innovative approaches.

Gareth Pearson (NERL-Las Vegas) presented a summary of Superfund-related research being conducted at the National Environmental Risk Laboratory (NERL). He said that two of NERL's seven divisions–Athens and Las Vegas–are involved in Superfund research. Las Vegas has been involved since 1980. NERL's mission and strategy is to build a strong program in measurements and exposure methods.

Pearson summarized NERL's research areas and products and noted that the emphasis has been on geophysical techniques, particularly for investigating NAPLs. To aid its research, NERL plans to build a controlled-spills facility, but has not yet selected a site. Research on sampling methods has focused on VOCs and soil; however, Pearson noted that the focus is now shifting toward SVOCs and issues of natural attenuation.

NERL also has been conducting research on screening and field analytical methods, such as x-ray fluorescence (XRF), enzyme-based biosensors, and immunoassays, because of the need for reliable field-portable technologies. Pearson also said that NERL is trying to shift support from sampling of contaminated soils to sample program design.

NERL provides technical support through the Consortium for Site Characterization Technologies (CSCT), the Environmental Photographic Interpretation Center (EPIC) in Reston, Virginia, and the Center for Exposure Assessment and Modeling (CEAM) in Athens, Georgia. Pearson asked that people write, call, or E-mail him with any questions.

Larry Reed (OERR) focused his presentation on the good news of Superfund and an update of Superfund reauthorization. He described Superfund as the environmentally "fail safe" part of EPA and cited the more than 500 construction completions as a measure of its progress. The goal is to clean up 80 sites this year, which would exceed the previous rate of 50-60 sites per year. Reed noted that statistics indicate that more than 90% of Superfund sites are complete or in construction, and cleanups are 20% faster and 20% cheaper than five years ago. He remarked that these successes are a tribute to RPMs, ORD, and others involved in Superfund.

Reed noted that Superfund recently completed its 5,000th removal and has screened and archived more than 30,000 sites for the program. Superfund is leveraging its resources to focus on the priority sites. It has excluded 15,000 *de minimis* parties from the process. Seventy-five percent of Superfund sites are PRP-lead, thus saving the program $12B. Each region has established an ombudsman to reduce involvement of headquarters.

A lot of resources have been removed from the front end of the Superfund process, so Superfund is working with the states to put sites on the NPL. An average of 20-30 sites are placed on the NPL per year. If a state objects to placing a site on the NPL, it can follow the issue resolution process.

Reed explained that the “bad news” about Superfund is that it is now in its third Congress for reauthorization and must be negotiated from year to year. Reauthorization has not been a bipartisan approach, and both parties have introduced bills on the program. Reed said that Tim Fields attended a recent oversight hearing. At this hearing, the GAO indicated that cleanups are taking four times as long as in the 1980s, but Fields explained that cleanups are actually proceeding *faster*.

Reed noted that there is potential for more hearings this year. A big issue that must be addressed is the expiration of the Trust Fund because remaining funds only will be sufficient for the next one or two years. However, Congress does not want to shut down Superfund and will fund it out of general revenues if necessary. The Administration wants to reinstate the Trust Fund because without the tax, there is a disincentive for prevention. In the interim, implemented administrative reforms have been well-received from the stakeholders. A legal group within Superfund has reviewed and basically approves of the reforms. Reed cited the Remedy Review Board and ROD reopeners as saving Superfund hundreds of millions of dollars.

In closing, Reed expressed appreciation for the tough job the TSP is doing. He commented that there has been a push for national consistency in the Superfund program, but flexibility is also needed because Superfund is a site-specific program. Reed explained that this is why the RPMs are encouraged to work with the Regional Centers. Reed also mentioned that another administrative reform is the push for consistency in risk assessments. A workgroup has been formed to develop a format for reporting risk assessment data. Finally, Reed said that the benefits of the Superfund program must be demonstrated, and noted that CERCLIS3 will help provide data to Congress, thus minimizing impact to staff.

PERMEABLE REACTIVE BARRIERS

Permeable Reactive Barriers: Status of Research and Development

Bob Puls (NRMRL-Ada) summarized the current status of research and development of permeable reactive barriers (PRBs) for treating contaminated ground water. He explained that the research and development of zero-valent iron PRBs for treating chlorinated solvents and chromium contamination is complete, but long-term performance issues remain and technology transfer is needed. Puls noted that these issues are being addressed by the Research Technologies Development Forum (RTDF). Research and development for the treatment of other contaminants and the use of other reactive media are underway. The reactivity of the media is being improved to enhance the kinetics of reactions, and alternative emplacement techniques (other than continuous wall and funnel and gate methods) are being developed to construct deeper PRBs. In addition, other applications of PRBs are being investigated, such as: use in source areas, surface treatment, and leachate treatment at landfills; use as a containment structure; and use with other technologies in sequential treatment.

Puls listed numerous *in situ* pilot demonstrations and 12 field demonstrations of the EnviroMetal (iron wall) Process. Emplacement methods for the pilot demonstrations include funnel and gate, Geosiphon, mandrel, vibrated beam, and jetting; however, the field demonstrations consisted of fewer funnel and gate constructions and more continuous iron walls.

Puls said that there is a three-fold challenge for the development of PRBs for the treatment of chlorinated solvents and chromate:

- reduce installation costs;
- demonstrate that O&M requirements are indeed low; and
- determine how long the walls will last.

The average installation costs for PRBs have decreased from $775K in 1997 to $440K in 1997 due to a decrease in the cost of iron and the development of easier emplacement techniques. Puls presented a table showing that the estimated cost to construct a wall 100-ft long, 30-ft deep, and 1.8-ft thick can range from $296K for a bioslurry trench to $537K for a funnel and gate construction. (These totals include the costs for mobilization, construction, and iron.) Comparison of iron wall remediation to traditional treatment methods shows a cost savings of approximately $3.7M, primarily due to lower O&M costs.

A continuous iron wall (150-ft long, 24-ft deep, and 2-ft thick) was constructed in Elizabeth City, North Carolina, in June 1996 to treat ground-water containing 10 ppm TCE and 10 ppm chromate. The objectives of the Elizabeth City demonstration were to conduct a full-scale demonstration of PRBs for mixed wastes; develop performance monitoring guidelines; and provide initial data for long-term performance assessment. The chromate plume at Elizabeth City is thin in its vertical dimension. It is migrating from a plating shop toward the Pasquotank River. The continuous wall was excavated and emplaced in just six hours using a trencher.

The wall was constructed at a cost of $500K, and serves to treat both the chromate and TCE contamination. The chromate ion reacts with the iron wall and water and is transformed to less soluble chromium hydroxide. The TCE is being degraded as designed and the appropriate by-products (ethene and ethane) have been observed downgradient of the wall.

The estimated annual cost of ground-water monitoring is $50K. Monitoring is being conducted using multilevel samplers parallel to the plume axis. In addition, angle cores have been collected through the iron wall to see where the transformations of contaminants were taking place. Most of the transformation of chromate to $Cr(OH)_3$ was observed to occur in the transition zone before the iron wall and within the first one inch of the wall. The downgradient portion of the angle core was green, due to reducing conditions that formed.

The significance of the work at Elizabeth City was that the demonstration became a model for other efforts, especially in terms of interaction with the stakeholders through the RTDF. Furthermore, the continuous wall design was demonstrated to be more effective in capturing and treating the plume. The site has become a focal point for demonstrating the success of PRBs.

Puls said that NRMRL has proposed further PRB research, which will focus on the long-term performance of PRBs, other reactive media and other contaminants, biogeochemical barriers, and monitoring issues. NRMRL is working with other groups and organizations to test PRBs at six sites.

Fry Canyon Permeable Reaction Wall Case Study

Randy Breeden (Region 8) and Paula Estornell (OERR) gave a presentation on a field demonstration at Fry Canyon being jointly conducted with EPA, U.S. Geological Survey (USGS), Bureau of Land Management (BLM), Department of Energy (DOE), GIPO, and the Utah Department of Environmental Quality (Utah DEQ). The demonstration involved the installation of a permeable reaction wall using three different reactive media at a uranium mill tailing site. OERR and ORIA provided the majority of funding for the project. USGS's Salt Lake

City Office provided overall project management, including the logistics for site characterization, field work, well installation, road construction oversight, wall installation, data gathering and analysis, and report generation. DOE and GIPO provided contractor support to Stan Morrison for analytical laboratory work and support, wall design, and performance analysis. BLM owns the land where the site is located, and provided in-kind services for road construction and surface preparation. In addition, BLM listed this site second on their National Performance Review. Utah DEQ issued and approved all necessary permits and has been very supportive of the project.

The site was chosen for a demonstration under Superfund and ORIA's efforts to find an inexpensive way to address radionuclide and metals contamination at the thousands of old mining sites and ore concentrator sites located primarily in the Western part of the United States. This field demonstration had three objectives:

1) Geochemical and hydrogeological evaluation of the site to determine its suitability for a demonstration of this type.

2) Design, installation, and operation of three selected barrier technologies (reactive media)

3) Evaluation of the barrier's performance and, if successful, evaluation of the commercialization of these technologies.

The site was operated intermittently from the 1960s to the 1980s. Prior to the demonstration, the wetlands located on the site had been inventoried for sensitive habitats, and a determination to protect the wetlands and riparian zones had been made. Archeological evidence indicates that the Anasazi Indians built cliff dwellings on the site and that other Native Americans may have used this site in the more recent past. Native Americans were consulted about the project and offered no objections.

Breeden noted that in order to conduct the site characterization, existing roads had to be rebuilt to get the drill rig onto the site. He then presented slides of the site and the barrier wall construction in August 1997. He noted that uranium concentrations of eight ppb were detected upgradient and 3,800 ppb downgradient of the contamination in the area where the reactive wall was to be emplaced. It was determined that approximately 11,000 liters per day would flow through the wall. After the site characterization was completed, wall installation began in August 1997.

Paula Estornell presented a video showing the emplacement of the wall. She noted that the wall was installed with phosphate, zero-valent iron, and amorphous ferric oxide (AFO). AFO was used because it can be jetted into the wall. Pea gravel was placed upgradient of the wall. Wall materials were placed a foot above ground water level. Backflow from the wall did occur, especially during flash floods.

Estornell noted that remediation results appear to be promising for all three materials used in the wall and that such a system appears to be a technologically and economically feasible option for passive treatment. Breeden said that next steps include continuing evaluations of the effectiveness of the wall and its life expectancy, studies on chemistry of the Bone Char, and possible injection of other contaminants upgradient to the wall to evaluate the ability of the reactive media compounds to remove them.

THERMAL TREATMENT TECHNOLOGIES

Engineering Forum Roundtable Discussion on Thermal Treatment

The Engineering Forum met with seven experts on thermal treatment to discuss issues associated with dynamic underground stripping, radio frequency heating, and thermal blanket/thermal well technology. A paper on this discussion is being developed by the Forum and will be published under separate cover from these minutes. For a copy of this paper, please contact the Engineering Forum Co-Chairs: Frank Vavra (Region 3), Steve Kinser (Region 7), or Bob Stamnes (Region 10).

How Heat Can Enhance *In Situ* Soil and Aquifer Remediation: An Overview and Guidance on Choosing the Appropriate Techniques

Eva Davis (NRMRL-Ada) noted that there are several limitations to conventional pump-and-treat and soil vacuum extraction techniques. Adding energy to the subsurface will lessen many of these problems by increasing vapor phase concentrations and mass transfer rates, lowering residual concentration levels in the subsurface, creating thermal gradients that cause the movement of fluids, increasing diffusion rates, and reducing the viscosity of NAPLs. This addition of energy can be accomplished by four different methods: (1) hot water injection; (2) steam injection; (3) resistive heating; and (4) radio frequency heating.

Davis explained that hot water injection is a displacement process that allows the recovery of contaminants as NAPL. It is effective in viscous material and causes changes in relative permeability of soils to favor oil recovery. A reduction in residual oil saturation results, and it leaves the contaminants in the soil amenable to bioremediation.

Steam injection is a displacement process that recovers liquids and enhances vaporization to allow the recovery of vapors. It is applicable to both shallow and deep contamination. Monitoring to detect steam zones is required. Cycling of steam injection with vacuum extraction has been found to be very effective. There are several full scale projects using steam injection that are completed or ongoing. Two specific methods of steam injection are Dynamic Underground Stripping, which recovers liquids and vapors, and Dual Auger Rotary Steam Stripping, which recovers vapors.

Resistive heating uses power line frequency current with electrodes that are placed in a circular pattern. Since soil is not appreciably electrically conductive, the electrical energy is dissipated to the soil as heat. Vapor is then extracted using SVE. Using power line frequencies, the current is carried by water, which limits the temperature to 100°C. Clay soils have been found to carry the current more effectively than sand.

Radiofrequency heating also is used in conjunction with SVE. Energy is applied to the soil in the radio frequency range using rows of electrodes or one long applicator. The energy applied is transmitted by the soil, allowing temperatures of up to 300°C to potentially be reached. However, the conversion of the energy from power line to radio frequency reduces efficiency. Radio frequency heating can also target clays.

Overall advantages of thermal methods are:
- They do not require the injection of chemicals.
- Low permeability zones are treated.
- They greatly reduce the time required for remediation and overall costs are reduced despite a large initial investment.
- There is a potential for destroying some contaminants *in situ*.

Questions and Answers

Davis was asked if the changes in permeability with steam injection are due to changes in clay mineralogy. Davis replied that the answer is not yet clear.

Another participant questioned whether steam injection has been used at shallow depths. Davis replied that steam injection for displacement is limited to deeper depths. She also noted that the steam pressure must be greater than the overburden. Otherwise the injected steam will come back up the well.

Davis was asked if resistive heating is limited by depth. Davis replied that it is known to work from the surface to an unknown depth.

Dynamic Underground Stripping

Roger Aines (Lawrence Livermore National Laboratory) explained that thermal remediation can be effective for several reasons: (1) it increases contaminant volatility; (2) it permits rapid mass transfer; (3) rapid diffusion and evaporation occur; (4) it decreases viscosity of water and contaminants; (5) and faster chemical reactions occur. He then explained Dynamic Underground Stripping (DUS). DUS is applicable to contamination below the water table. It combines steam injection with extraction wells by heating water to the boiling point, then using the vacuum from the extraction wells to decrease the pressure and allow boiling of the ground water. One major problem is that DUS is not applicable to less-permeable soils. In these regions, direct electrical heating must be applied. Electrical Resistance Tomography (ERT) is used for process control by imaging heat profiles based on depth.

Aines described a DUS project at a gas pad site at Lawrence Livermore National Laboratory. At this site, DUS was able to remove an average of 64 gallons per day of free product by cycling steam injection with vacuum extraction. Contamination did not spread during clean up, all contamination was removed from the vadose zone, and almost all free product was removed from the site. Two weeks after injection ended, active bioremediation was found to be occurring at temperatures as high as 90°C. The total cost for the project was \$25-50 per yd^3.

Aines then discussed a promising DUS project at Southern Cal Edison's Visalia Pole Yard site. Prior to thermal recovery efforts, conventional pump-and-treat efforts at Visalia were recovering approximately 10 pounds of hydrocarbons per week. In the first six weeks of thermal treatment, 29,400 pounds of vapor hydrocarbons were burned in boilers, 45,500 pounds of contaminant were destroyed *in situ*, and 200,000 pounds of free product were recovered.

Aines concluded by saying that DUS is promising for the remediation of free product source areas and can be used with hydrous pyrolysis oxidation (HPO), which is a process that destroys organics at steam temperatures. ERT provides excellent steam zone control for timing injection and extraction cycles. Lastly, the large-scale experience at Visalia Pole Yard has answered many cost and applicability questions.

Questions and Answers

Aines was questioned about the effect of steam injection on bacterial populations. Aines answered that there was not an in-depth evaluation of microbial populations, but that these populations were examined both before and after steam injection, and the populations were affected. Another participant asked Aines if biofouling was a problem. Aines replied that initially, biofouling was a problem.

In response to a question whether DUS had been done in clays, Aines replied no. Aines was then asked for the basis of the cost per cubic yard estimates. Aines replied that they were based on the area of soil heated at Lawrence Livermore National Laboratory.

A participant asked Aines if Visalia had problems meeting air emission standards . Aines replied that they did not because Southern Cal Edison Company had put an effective boiler system in place to destroy vapor-phase organics.

Aines was questioned on the issue of steam escape up through the ground surface from below. Aines replied that good process control (through the use of ERT) eliminates this potential problem.

Aines was then asked about the previous remediation systems at Visalia. Aines replied that three different pump-and-treat systems had been in place at Visalia before they switched to DUS.

Lastly, Aines was asked if DUS was significantly better than chemical treatment with peroxide. Aines replied that steam disperses more widely than peroxide, is able to penetrate into smaller cavities in the soil, and can conduct two to three feet into impermeable materials.

Visalia Pole Yard Remediation

Craig Eaker (Southern Cal Edison) discussed a Dynamic Underground Stripping (DUS) project to remediate DNAPL contamination, which has been in operation at Visalia Pole Yard during the past three years. First, he presented a table explaining the site's history:

1923-1980	Visalia Pole Yard Operated
1976	Ground water pumping initiated
1977	Grout wall completed
1985	Phase I water treatment plant
1985	Cal-EPA Superfund Site
1987	Phase two water treatment plant
1989	U.S. EPA Superfund Site Number 199
1992	Remedial investigation/feasibility study completed
1994	RAP/ROD
1995	Regulatory approval for DUS
1996	Design and construction
1997	Remedial action

Eaker next presented a list of the operation parameters for the DUS Process employed at the site:

- 200,000 lbs./hour steam introduced by 11 injection wells
- Vapor extraction by seven wells at 2,500 standard cubic feet per minute (SCFM) at approximately 20 in. mercury
- Vapor treatment—thermal oxidation
- Ground water extraction at 400 gallons per minute
- Ground water treatment—separation, filtration, and GAC
- Monitoring-ERT and thermocouple
- Product recovery tracking

Eaker noted that to date, more than 35,000 gallons of contaminant have been collected at the site, but the exact amount is difficult to assess, because most of it has been collected in the form of an emulsion. He noted that the site temperatures exceeded 80°C when using Electrical Resistance Tomography. Next, he presented a table to show how they tracked the DNAPL:

Free-phase:	Volumetric accounting of LNAPLS and DNAPLs from API and DAF separators
Vapor-phase:	Continuous hydrocarbon and CO_2 analysis of extracted non-condensable vapors.
Liquid phase:	Continuous hydrocarbon analysis of clarified extracted ground water and condensate

Eaker then presented a graph of cumulative gallons removed from the site and a graph depicting the vapor and aqueous phase removal equivalents to gallons of DNAPLs. He noted that large levels of contaminant removal could be detected using continuous emissions monitoring and measurements of total inorganic carbon.

Eaker next presented a chart showing the remediation goals for the site:

Parameter	Soil	Groundwater
Pentachlorophenol	17 ppm	1 ppb
TCDD (eqv)	1 ppb	30 ppq
benzo(a)pyrene	0	0.2 ppb

Eaker noted that a remedial investigation and feasibility study using enhanced *in situ* biological treatment conducted at the site would have cost approximately $45M net present value (npv), including about $7.5M of capital investment. Approximate DUS costs were much less. For example, a 10-year DUS demonstration was estimated to cost $22M (npv); a 5-year demonstration—$17M (npv); and a 2-year demonstration—$14M (npv). Eaker then noted that they conducted one- and two-dimensional tests for the site, but a three-dimensional test was not performed because it would have required development of a computer model. Eaker noted that completion of the demonstration is expected in two years.

Eaker explained that steam operations at Visalia are funded through March 31, 1998. At this time, the intermediate aquitard is still being treated, and surfactant injection is being evaluated. At the end of the steam process, compliance issues will be addressed.

Questions and Answers

In response to a question from Vince Malott (Region 6), Eaker noted that there were 29 ERT monitoring wells, 13 targets for ERT, and 13 thermocouples. He added that ERT provides the ability to view the site three-dimensionally.

INNOVATIVE ENVIRONMENTAL REMEDIATION TECHNOLOGIES

Decision Analysis for Remediation Technology

Kevin Kostelnik, INEEL, noted that INEEL develops and evaluates innovative remediation products using an *in situ* stabilization system and “Decision Analysis for Remediation Technology” (DART), which is a contaminant mapping system that provides real time feedback.

The DART system is an integrated tool (computer aided system) that was developed to analyze DOE subsurface contaminants from landfills, plumes, and ponds at more than 600 waste sites. It includes site characterization and analysis data, site specific technology requirements, performance and benefit models, industrial and DOE technology descriptions, presentation and report generators, and operator interfaces. More specifically, DART provides the following: summary information on the site data, calculation of site risk, calculation of site priority, list of specific technical requirements, site specific clean-up criteria, list of industrial technologies and/or government development technologies, relative cost of technologies, and measures of effectiveness and implementability.

The contaminant mapping system was developed to enhance control of hazardous remediations. It is set-up on a conventional excavator that deploys multiple sensors during hazardous excavations, provides real-time characterization that can improve decisions and productivity, and reduces waste volume, assay, and treatment costs. The system includes a stable sensor platform, real-time mapping capability, a radiofrequency data link, laser rangefinder positioning, and chemical, radiological, and geophysical sensors.

Kostelnik noted that the contaminant mapping system is being implemented at a project on the Erie Canal in Ohio to validate *in situ* measurements using side-by-side comparison of sensors and counts versus concentration. Monte Carlo modeling with CYLTRAN and Geometric and Spatial Resolution is being used at the site. Plans include development of an ANSI certified standard for *in situ* real-time field measurements.

Kostelnik next described INEEL's *In Situ* Stabilization System, was successfully demonstrated at the INEEL Acid Pit in September 1997. The system was developed to enhance the ability to immobilize and treat contaminants in place. It can to eliminate contaminant migration, reduce environmental risks and remedial costs, control or eliminate contaminant exposure during operation, and provide a long-term and an interim solution.

VOC REMEDIATION

Development of Biofilters for the Removal of Chlorinated VOCs from Off-Gas Streams Created During Environmental Remediation

Brady Lee (INEEL) discussed the development of biofilters to remove chlorinated VOCs from off-gas streams created during environmental restorations. He explained that INEEL became interested in addressing chlorinated VOCs because they pose large problems at many sites. According to Lee, 60-70% of future remediations will be conducted to cleanup contaminants with chlorinated mixtures. Below is an abstract of Lee's presentation:

Vapor phase bioreactors, such as biofilters and biotrickling filters, represent alternative air pollution control technologies that remove highly chlorinated contaminants such as carbon tetrachloride, TCE, and perchloroethylene (PCE) from off-gas streams. These contaminants are currently removed from off-gases using carbon adsorption or thermal oxidation. While both technologies are effective, they can be expensive to operate and can cause further environmental problems. In biofilters, contaminants such as carbon tetrachloride and PCE are removed by reduction rather than oxidation, which also is the mode of removal in classic vapor phase bioreactors, while compounds such as TCE can be removed cometabolically using propane as the primary carbon and energy source. The feasibility of anaerobic carbon tetrachloride biofiltration using compost-based biofilters and cometabolic biofiltration of TCE is presented below.

In a case study, biofilters were operated for approximately nine months using hydrogen and carbon dioxide as the electron donor and carbon source respectively. Methanogenic conditions were established after approximatelyonemonth of exposure to nutrients. An empty bed contact time (EBCT) of approximately 2.5 minutes was used for testing. Upon exposure to carbon tetrachloride, the biofilters were able to remove over 80% for most of the test period. Overall removal efficiency ranged from 60-95% for biofilters receiving hydrogen and carbon dioxide as nutrients.

Testing with laboratory-scale biofilters also indicated that cometabolic removal of TCE from vapor streams using gas phase bioreactors was possible. Using propane as the cometabolic primary substrate, indigenous bed medium microorganisms were able to remove up to 93,000 mg of TCE at an inlet concentration of 6,400 mg of TCE, when bed medium moisture content was at the optimal level. Biofilters were operated at an EBCT of two minutes.

Laboratory testing indicated that vapor phase biofilters, whether operated under aerobic cometabolic conditions or under anaerobic conditions, represent an operationally-feasible alternative to currently used vapor treatment systems. Further testing is needed to determine the effect of mixed contaminant streams on removal of the target contaminant.

Questions and Answers

In response to a question from Ken Lovelace (OERR) on whether Lee would consider combining liquid and vapor phases for biofiltration, Lee noted that he would consider this for biotrickling filters. In response to a question from Mark Ferrey (Minnesota Pollution Control Agency), Lee said no sterile controls were used in his study to measure biodegradation.

In response to another question on breakthrough from Lovelace, Lee noted that contaminants always were recoverable, except when conditions became too acidic.

Ultraviolet VOC Destruction Technology

Ted Weigold [Founder and President of Process Technologies Inc. (PTI)] presented information on his company's Photolytic Destruction Technology (PDT). PDT is a method of photochemically oxidizing gaseous halogenated VOCs as they flow through a reaction chamber. It uses low pressure ultraviolet (UV) lamps, with UV emissions primarily at wavelengths of 185 and 254 nanometers, located inside the reaction chamber. Photons emitted from these lamps are absorbed by the target chemicals, resulting in the breakdown of the molecules. The resulting by-products are chemically reacted with a solid reagent to form non-hazardous salts.

According to Weigold, PTI has proven that the technology is preferentially suited to destruction of low-flow, high concentration, gas streams. However, high-flow, low concentration gas streams also can be handled by PTI’s process by removing the VOC contaminants from the gas stream using a concentrator. Readily available accessory technologies are used to strip VOCs from water and soil. The resulting gases can be destroyed by the PDT, which is capable of destroying mixtures of chlorinated and non-chlorinated VOCs. PDT has been used at McClellan Air Force Base (AFB) for an SVE removal action and at Hill AFB for a tank vent off-gas treatment. In addition, PDT, in combination with a fluid-bed concentrator, has been demonstrated at NAS North Island to treat SVE off-gas and to compare its effectiveness to granular activated carbon treatment and catalytic oxidation.

Weigold concluded that PDT can be applied at the following types of sites:

- Process Tank and Building Vents
- Chemical Production
- Plastics Production
- Pharmaceuticals
- Water Remediation
- Soil Vapor Extraction

- Paint Booths

Weigold then encouraged the group to contact him if anyone knows of a site where this technology may be effectively applied.

SOIL VAPOR EXTRACTION

SVE Systems: When to Shut Them Off

Jim Cummings (TIO) and Dominic DiGiulio (NRMRL-Ada) discussed SVE systems and offered suggestions for determining when to discontinue their use. Cummings observed that SVE is used for extended periods of time. For example, one site has been using SVE for over 10 years. Part of the difficulty in using SVE is knowing when to "quit." There is a lack of uniform, defined criteria for determining when and how to stop using SVE, and little information is available on monitoring methodologies. Cummings noted the Forum produced an issue paper on SVE several years ago, but indicated more information is needed. He suggested that there is a need for a lessons-learned document highlighting ten or 12 rules for managing and monitoring SVE projects. He also suggested that a standard quarterly report format or closure report format would allow the program to accumulate and compile more information on SVE projects as well as any technology. Over the next year, he indicated these issues will be addressed.

DiGiulio distributed a report, "SVE Closure: Assessment of Mass Flux to and From Ground Water," and asked audience members to review and comment on the document. He asked that comments be submitted by February 27, 1998. He summarized the report during the remainder of his presentation. The abstract, reprinted from his report, is provided below.

> "Site closure for soil venting application typically requires attainment of specified soil concentration standards based on the premise that mass flux to ground-water not result in exceedance of Maximum Contaminant Levels (MCLs). Unfortunately, realization of MCLs in ground-water appears unrealistic at many, if not most, sites. This results in soil remediation efforts which may be in excess of what is necessary for future protection of ground-water and soil remediation goals which often cannot be achieved within a reasonable time period. Soil venting practitioners have attempted to circumvent these problems by basing closure on some predefined percent total mass removal, or an approach to a vapor concentration asymptote. These approaches though are subjective and influenced by venting design. We propose an alternative strategy based on assessment of five factors: (1) site characterization, (2) design, (3) performance monitoring, (4) rate-limited vapor transport, and (5) mass flux to and from ground water. Demonstration of closure is dependent on satisfactory assessment of all five factors. In this paper we focus on assessment of mass flux of chemicals to and from ground water using an analytical model we term VFLUX. VFLUX is similar to the well-known model VLEACH, except that it allows time dependent boundary conditions at the water table interface which is the centerpiece of our mass flux approach because it dynamically links performance of ground-water remediation to SVE closure. Substantial progress in remediating ground-water translates to increasingly stringent soil venting performance standards while lack of progress in remediating ground-water translates into minimal soil venting application."

LANDFILL CAPS

Cap Guidance Developed By Region 1

Jean Choi (Region 1) reviewed "Alternative Cap Design Guidance Proposed for Unlined, Hazardous Waste Landfills in the EPA Region 1," which was issued on September 30, 1997. He distributed a copy of the guidance and discussed the key points of the proposed guidance. Landfill caps at Superfund sites should meet RCRA Subtitle C requirements. Caps should be constructed with relatively permeable materials for most Superfund sites. To minimize the introduction of rain into the landfill, the Region recommends a multi-layer cap. The Region developed the guidance because it is experiencing several landfill failures. Last year, eight of the failures were due to caps, of which many were constructed of clay. The Region found that clay caps often dry out, are difficult to maintain, are prone to cracking, and sometimes adhere to the membrane. The Region currently does not recommend compacted clay for capping. Choi reviewed additional reasons for cap failures. These include:

- inadequate interface friction for multi-geosynthetic lined slopes;
- damage caused by equipment loads and seismic forces;
- rain seepage and its impact on slope instability during or after intense rain; and
- the current design methods (HELP) that greatly underestimate flow quantity.

To address these problems, the Region recommends updating cap requirements for Superfund sites; using the alternative cap design proposed by the Region; and using only qualified engineers to design the cap. The alternative cap design consists of drainage geocomposite, geomembrane, and 10^{-4} cm/sec soil (or geosynthetic clay liner on top of flat areas). An evaluation of this alternative cap using the HELP model shows that it can provide equal or better performance minimizing the infiltration of rainwater than an EPA cap recommended to meet the requirements of RCRA Subtitle C. This new guidance has been used at several sites for which landfills will be constructed this year.

Contact either Dennis Gagne (617-573-9661) or Jean Choi (617-223-5505) for a copy of the proposed guidance or for more information.

IN SITU CHEMICAL FLUSHING/SURFACTANTS

***In Situ* Flushing/ Surfactants**

Lynn Wood, NRMRL-Ada, discussed enhanced source removal using *in situ* chemical flushing. He defined *in situ* chemical flushing as the passage of fluid containing chemical adjuvants through contaminated soils or aquifers to facilitate contaminant removal by enhanced mobility and solubility. This process entails four different types of flushing: 1) surfactants; 2) cosolvents; 3) surfactant/cosolvent mixtures; and 4) macromolecular complexation. As evidence of the viability of this process, Wood cited a demonstration at Hill Air Force Base (AFB) where the injection of a starch molecule resulted in the partition of contaminants.

This technology is applicable in source areas, unconsolidated permeable formations, and sparingly soluble organics. The technology has been proven to be feasible on a small-scale field demonstration. However, scale up testing is needed. The key issues are:

- Economic Feasibility—Currently, there is limited cost information available. The largest cost items are adjuvant waste management and recycling. A cost comparison with other approaches is needed.
- Performance Criteria—A determination needs to be made whether environmental standards or risk measures are the most appropriate criteria. Also, a decision about whether to evaluate the source or the site as a whole needs to be made. The criteria also must address the impact on site remediation.

- Performance Assessment—Impacting performance assessment is the lack of NAPL characterization protocols, availability of multiple approaches, and the consistency of the assessment process.
- Source Delineation—During the Remedial Design, the source and extent of NAPLs need to be adequately defined to design an appropriate remediation approach. This will impact the remediation performance assessment.
- Mobility Control—The remedial fluid control process must be adequately controlled through “good engineering.” This will prevent the spread of DNAPLs into uncontaminated areas.
- Technology Coupling—For source remediation, it may not be practical to remove all of the contaminant mass through one process. Other technologies may need to be used to complete remediation efforts.
- Adjuvant Recovery and Reuse—This process needs to establish adequate control and recovery processes of injected fluids. This requires the separation of the adjuvant from the contaminant and the reinjection of the adjuvant.

The technology has been demonstrated at several sites, including Fredericksburg, VA, Piketon, OH, Hill AFB (OU2), and Hill AFB (OU1). The results varied from zero recovery at Fredericksburg because of hydrogeology problems to 90% recovery at Hill AFB (OU2) where surfactant solubilization with mobility control was used to address TCE. Some of the methods used to assess the pilot demonstrations included core sampling, groundwater sampling, and effluent monitoring.

METHYL-BUTYL-ETHER (MTBE)

Remediation of MTBE-Contaminated Water

Matt Hagemann (Region 9) provided an overview of literature on transport and clean up of MTBE-contaminated groundwater. Hagemann noted that MTBE was first introduced in 1979 to boost fuel octane. In 1990, the use of MTBE as a fuel oxygenate was increased when the Clean Air Act Amendment required the use fuel oxygenates to reduce CO_2 and ozone.

Hagemann noted that in Santa Monica, 27% of all shallow wells and springs in eight urban areas were contaminated with MTBE and that MTBE has been most frequently detected in Denver, the Northeast, and the Dallas/Fort Worth areas. It has been detected in 51 drinking water systems, but at lower contaminant levels. MTBE is the third most-frequently detected VOC after chloroform. Its health hazard is currently unknown, but is believed to be a possible human carcinogen; rat studies are being conducted to determine this. EPA has issued an advisory on MTBE and wants to develop a research compendium to identify current areas of research and priority areas for more research.

MTBE will partition readily to the vapor-phase in the unsaturated zone and to the aqueous phase in the saturated zone. However, it will not readily sorb to soil. MTBE is very soluble in water and has a very low affinity for organic carbon and no retardation; it does not appear to readily biodegrade.

In soil, MTBE can be remediated using SVE, which causes MTBE to readily volatilize from free and residual phases; this process is most efficient in dry soils. In ground water, MTBE can be remediated with air sparging and SVE, *in situ* biodegradation, and pump-and-treat. The effectiveness of air sparging and biodegradation at the field scale is unclear. However, a study at the CFB Borden site has tentatively concluded that biodegradation has reduced MTBE mass significantly without degradation of by-products. Loss of MTBE mass at a Long Island site has not been demonstrated.

There are *ex situ* alternatives for MTBE sites, which include air stripping, advanced oxidation, adsorption, and GAC fluid bed reactor. With air stripping, off-gas treatment may be required. Advanced oxidation alternatives include UV/hydrogen peroxide, UV/ozone, hydrogen peroxide/ozone and Fenton's reagent. Advanced oxidation of MTBE requires relatively long contact time and twice as much energy as that for aromatic hydrocarbons. In addition, it may produce toxic by-products. Adsorption alternatives include GAC and synthetic resins. However, the GACs' life expectancy for MTBE is reduced by 90% when compared to that for aromatic hydrocarbons. A GAC Fluid Bed Reactor can provide aerobic degradation and carbon adsorption in one reactor. However, cultures must adapt for improved efficiency.

The estimated cost for MTBE remediation ranges from 1.3 to 7 times that for fuel sites without MTBE. The estimated cost for reducing 1,000 ppb MTBE to 35 ppb equals $1,000 per gallon.

Remediation of MTBE-Contaminated Water

Matt Hagemann (Region 9) provided an overview of literature on the transport and cleanup of MTBE-contaminated ground water. He focused on Region 9's perspective of the issue, because of the wide-spread use of MTBE in California.

U.S. EPA's Air Program advocates the use of MTBE as an oxygenate in gasoline. Not all states use it, however, opting instead for other ethers or ethanol. Other states just use MTBE in winter fuels. MTBE is the second most produced chemical in California fuels. California requires the use of MTBE in its fuels, and MTBE makes up 3.5% of the fuels in the U.S.

In Santa Monica, California, up to 610 ppb MTBE were detected in a drinking water well field, which exceeds the 20-40 ppb advisory limit. The advisory limit is based on taste and odor. There are no health-based standards for MTBE, and no human health studies exist—just extrapolations from rat studies. In New Jersey and New England, MTBE is the second-most detected VOC after chloroform; however, only 3% of MTBE detections exceed 20 ppb. Due to the number of sources and the volume of the chemical, more releases of MTBE are expected in the future.

MTBE is used in fuels to meet Clean Air Act requirements, but is listed as a CERCLA hazardous substance in the Clean Air Amendments. Its relatively high vapor pressure is indicative of its ability to readily partition into the vapor phase in the unsaturated zone. MTBE is a polar molecule that is held tightly by water and is 20 times more soluble than benzene. As a result, it will readily partition to the aqueous phase rather than the soil. It has a low log K_{oc} (even lower than benzene), so it has a negligible retardation in the subsurface. In addition, MTBE does not appear to readily biodegrade in the subsurface.

Remediation alternatives for MTBE in soil are limited to soil vapor extraction (SVE), which can readily volatilize MTBE from free and residual phases, but is most efficient in dry soils. Remediation alternatives for ground water include air sparging with SVE, *in situ* biodegradation, and pump and treat. The effectiveness of air sparging with SVE is unclear because MTBE is highly soluble, it has a low Henry's Law constant, and is not readily biodegraded. The effectiveness of *in situ* biodegradation is also uncertain at the field scale. For example, biodegradation has been shown to significantly reduce the mass of MTBE at the CFB Borden site, and no degradation by-products were observed. On the other hand, mass reductions were not demonstrated at a site on Long Island.

Pump and treat is currently the most effective method for treating MTBE-contaminated ground water. Once the ground water is extracted, it can be treated *ex situ* by air stripping, advanced oxidation, adsorption, or using a granular activated carbon (GAC) fluid bed reactor. The low Henry's Constant and high solubility of MTBE dictate a high air-to-water ratio for air stripping that is typically ten times higher that those required for aromatic hydrocarbons. Treatment of the air stripping off gas may be required. Treatment of contaminated ground water by advanced oxidation requires a relatively long contact time, and the energy required is twice that for aromatic hydrocarbons. Adsorption is another option for treatment, and alternatives include GAC and synthetic resins. However, GAC life expectancy is 90% shorter for MTBE than for aromatic hydrocarbons. GAC fluid bed reactors incorporate aerobic biodegradation and carbon adsorption in one reactor. They have been shown to be effective in reducing 500 gpm influent concentrations from 900 ppb to 40 ppb at a site in Nevada.

The costs of treating MTBE sites are estimated to be 1.3 to 7 times greater than sites without MTBE. The estimated costs for reducing 1,000 ppb MTBE to 35 ppb range from $1-4 for every 1,000 gallons for GAC fluid bed reactors to $5 to 15 for every 1,000 gallons for advanced oxidation or adsorption by GAC.

The State of California will complete a risk benefit analysis for MTBE treatment this year. By the summer of 1999, the State will have an estimate of a maximum contaminant level for MTBE.

IN SITU STABILIZATION

In Situ Stabilization of the INEEL Acid Pit

Guy Loomis (INEEL) discussed an *in situ* stabilization treatability study conducted in 1997 at an acid pit located on INEEL's Radioactive Waste Management Complex. The acid pit is a shallow contaminated mixed waste soil region in the subsurface disposal area. It is 17 feet deep with the top five feet primarily contaminant-free. The main contaminant of concern is mercury, but trace amounts of Cs-137, Pt-239, and U-235 have been found. Most contaminants are located in the bottom three to six feet of the pit.

The treatability study involved both cold (non-contaminated area) testing and actual acid pit stabilization. Cold testing occurred in different soil pits with multiple field trial columns, destructive examination, and set parameters for the acid pit, which included jet grouting at 6,000 psi. Results indicated that low viscosity produces better columns and fewer grout returns, and no contamination spread away from grouting area.

The actual acid pit *in situ* stabilization project involved jet grouting the site to create a monolith. The grout used was TECE (a proprietary iron oxide cementatious grout material) applied at 6,000 psi grout pressure. Emissions were controlled with shrouds, thrust blocks, and HEPA filters. The criteria of success established for acid pit stabilization included:

- cores that pass TCLP protocol for mercury
- cores that display resistance to subsidence (compressive strength at least 60 psi)
- cores that display resistance to degradation
- no spread of contamination to the surrounding region

The acid pit was stabilized in a single week of grouting. A total of 53 boreholes were injected with a total 3,400 gallons of grout in four days. Air filters and smear samples were taken to evaluate the contaminant spread.

Preliminary results indicate that:

- The process can be fully implemented at a "hot" controlled site.
- All major drilling equipment was released from site.
- Clean out of system produced no secondary waste (water released).
- There was difficulty with grout returns on the third and fourth days of grouting

- Assuming a treated volume of 14 x 14 x 8 feet, voids can be filled at 30%.

The grouted acid pit will be cored in March 1998 and results should be available by September 1998.

BIOREMEDIATION

Isolation of Anaerobic Bacteria from an Aseptically Cored Well (TAN 34) in the TCE Plume at the Test Area Site of INEEL

Ron Crawford (INEEL) discussed a project being conducted at INEEL's Test Area Site (TAN34) to examine intrinsic bioremediation of TCE. TAN 34 is an area of fractured basalt with 1,000-2,000 ppb TCE contamination. Aseptically-collected cores were collected from the site, from which aerobic and anaerobic bacteria was isolated, cultured, and analyzed for their DNA and ability to degrade TCE. 450 cultures were prepared, from which 107 bacteria isolates were found. Using a TCE screening process, 30 of these isolates were identified as being able to degrade TCE.

Crawford noted that future work will include further bacteria isolation and characterization, as well as another TCE screen with and without electron acceptors. Degradation and kinetic study development is planned for February.

Questions and Answers

In response to a question from Jon Josephs (Region 2), Crawford noted that the conditions were already anaerobic at the site, but that most work was conducted in a more aerobic portion of the plume. He then said that spores were not specifically looked for, but that conditions at the site are very "starved," so the microorganisms grew very slowly. He added that they only looked at what was happening in the low nutrient portions of the plume, but could consider adding nutrients if growth was too slow. However, if too much biofilm is grown at a site, it can "plug-up" the system.

In response to a question from John Wilson (NRMRL-Ada) on what drives dechlorination, Crawford indicated that he thinks that most dechlorination at the site occurs near the injection wells, where a lot of raw sewage was injected.

Biodegradation of Solid Explosive Fragments Within a Soil Matrix

Corey Radtke (INEEL) presented a summary of INEEL's research into treatment of soils containing chunks of TNT. An abstract written by Radtke and Frank Roberto (INEEL) is provided below:

Explosives contaminated soil at the Idaho National Environmental and Engineering Laboratory (INEEL) includes areas containing chunks of explosive material from unexploded and partially exploded ordnance. The chunks present technical and safety challenges in the remediation of the site. TNT is only slightly soluble in water, while biological transformation of the TNT occurs primarily in aqueous solution, and probably to a lesser extent at the solid interface. Remediation is therefore limited by the bioaccessibility of chunk TNT. An effective field-applicable treatment requiring a minimal handling of explosives chunks was developed.

We pretreated the soil with a minimal acetone slurry followed by evaporation to dissolve and redisperse solid TNT before applying remedial treatments. The well-described treatments of anaerobic slurrying and composting were then applied to untreated and acetone pretreated soils. Acetone pretreated soils responded to the applied bioremediation treatments significantly better than untreated soil. Acetone pretreatment followed by anaerobic slurries showed a greater than seven-fold increase in monoamine production after 14 days of incubation as compared to untreated soil, with corresponding disappearance of extractable TNT from 1,800 ppm to 976 ppm (untreated) and 2,800 ppm to 8.3 ppm (treated). Composting microcosms at 55°C showed sporadic removal from 3,000 ppm to 300 ppm in 24 days for untreated soil while pretreated soil demonstrated conclusive removal from 3,000 ppm to 18.1 ppm in six days. The superior removal rates and efficiencies in the acetone pretreated systems are likely due to the increased availability of TNT to the degrading microorganisms. We conclude that minimal solvent pretreatments can make chunk TNT in TNT-contaminated soil redistribute into a system which can be effectively treated by biological methods. Development is underway toward applying the minimal solvent pretreatments in the field.

Evaluating Natural Attenuation and Enhanced Bioremediation of Trichloroethene in Fractured Basalt

Kent S. Sorenson, Jr. (INEEL) presented an overview of the Test Area North site at INEEL, an industrial complex where from 1955 to 1972, liquid industrial waste was injected into the water table at a depth of approximately 200 feet via an injection well. In the early 1990's, an RI/FS was conducted to determine the boundaries of the plume, which was found to reside at depths of 200 to 400 feet, and possessed a length of over two miles. Concentrations of TCE are as high as 5,000 μg/L, with higher concentrations present at shallower depths. In 1995, a ROD was signed. The default remedy was pump and treat combined with hydraulic containment. However, the ROD also identified innovative technologies, including natural attenuation, *in situ* bioremediation, and *in situ* chemical oxidation.

Ground water monitoring has not shown the significant plume growth predicted by the model, nor has it shown significant concentration increases in distal or near-source monitoring wells. This implies that degradation may be playing a significant role in the remediation of the plume. In order to evaluate this possibility, a conceptual model of site containment behavior is needed for the prediction of transport. In addition, field data are necessary to show attenuation relative to predictions. Lastly, an identification of mechanisms responsible for attenuation must be made.

The site conceptual model assumes a continuous, fixed source of TCE with an original disposal of between 500 and 35,000 gallons. It also assumes that no degradation of the plume is taking place, and uses numerical modeling from the RI/FS. However, this constructed model does not agree with the reality seen at Test Area North. Instead of a very dense source area and diffuse outer boundaries consistent with no degradation taking place, the source area is significantly less dense. If the model is modified to include a 12-year half-life for the TCE, the model much more closely agrees with observations made. Possible attenuation mechanisms are: (1) dispersion; (2) sorption; (3) anaerobic reductive dechlorination; and (4) aerobic degradation of daughter products. Dispersion may be significant at large distances from the plume, but does not explain the lower concentrations near the source area. Sorption can be dismissed because of the very low organic content of basalt. In evaluating the two remaining possibilities, DCE concentrations were examined. DCE could be a co-contaminant or daughter product of TCE degradation. However, DCE concentrations are highest near the source, then drop off sharply with distance. This would suggest that anaerobic reductive dechlorination is taking place, with electrons being donated by the sludge close to the source area. This DCE is then degraded down gradient in aerobic conditions.

The natural attenuation that is taking place implies that if flux from the source area can be reduced, the plume will contract as a result of simple mass balance. Bioremediation may be a possible mechanism for this reduction in flux. An experiment using a crushed core and lactate indicates that TCE is being degraded, and that the daughter DCE is quickly being degraded to ethene and ethane. Further tests are necessary to determine if enhanced bioremediation combined with natural attenuation provides a viable alternative to more aggressive approaches.

Questions and Answers

Sorenson was asked to explain the macroscale dispersivity data presented. Sorenson answered that the data came from large-scale modeling across INEEL combined with calibration.

Kay Wischkaemper (Region 4) asked whether Sorenson thought the plume was sinking. Sorenson noted that the presence of a confining sedimentary bed with lateral continuity has prevented significant contamination of lower bedrock. In addition, the annual precipitation in this portion of INEEL is approximately nine inches.

Analysis of Intrinsic Bioremediation of Contaminated Aquifers

Allan Wylie (University of Idaho/Lockheed Martin Idaho Technologies Company) presented borehole evidence for intrinsic bioremediation at the Test Area North site within INEEL. Organic compounds and radionuclides from a wastewater injection well in operation from 1953 to 1972 have contaminated ground water near the Test Area North site. The areal extent of the contaminant plume is about one square mile with contamination extending 10,000 feet from the injection well. As part of the analysis, two boreholes were drilled 50 feet apart within the plume, with the holes penetrating about 200 feet of the underlying Snake River Plain aquifer. Correlations between the two wells were developed using rock geochemistry, radar tomography, borehole televiewer logs, and standard geophysical logs. One of the wells was drilled aseptically to collect microbiological samples.

Higher concentrations of TCE were found at shallower depths due to the more fractured nature of the bedrock. Conversely, PCE concentrations were lower at shallower depths. One possible explanation for this anomaly is that PCE degrades anaerobically, an environment which exists at shallower depths due to the waste water injection. PCE concentrations increase with depth as the environment becomes aerobic due to lower concentrations of the particulate matter waste. Concentrations of trans DCE, a product of microbial processes, also were greater at shallow depths. Compounds that favor microbial growth, such as dissolved oxygen, nitrate, and sulfate, are more abundant at shallower depths. Corresponding to this shallow zone is a thermal anomaly, with the upper half of the aquifer approximately 2°F warmer than the lower portion, with higher temperatures closer to the former injection well.

Contaminant, chemical, and thermal stratification is present in two boreholes drilled near the Test Area North site. In order to better characterize possible intrinsic bioremediation that may be occurring, future research should encompass heat-flow modeling, more Cl/Na mole ratios to evaluate the possibility of TCE dechlorination, isolation of microbes which degrade TCE, and push-pull tests.

Questions and Answers

Wischkaemper asked Wylie if methane or carbon monoxide were detected in the two wells. Wylie responded that these compounds were not analyzed, but that he would like to do so in the future because they are products of respiration.

Wylie was asked about the screen separation used in the wells. Wylie responded that the wells were drilled in the Fall of 1996, and tests were performed in the Summer of 1997 with a minimum screen separation of 10 feet.

MODELING

Soil and Ground Water Modeling of Creosote Components and PCP at the Texarcana Wood Preserving Company Superfund Site

Ron Arnett (INEEL) discussed soils and ground water modeling of creosote components and PCP at the Texarcana Wood Preserving Company Superfund Site. He explained that the site operated in the 1950s and 60s as an old process area for the wood treating plant. In 1984, the company went out of business and in 1986, the site was listed on the National Priorities List. A remedial investigation was completed in 1991 and a ROD written in 1992. The ROD proposed on-site thermal destruction for the contaminated soils and pump-and-treat for the contaminated ground water. Other remedial methods considered for the site included a cap and immobilization for the soils and hydraulic barriers and natural attenuation for the ground water.

Arnett noted that a simple, preliminary model was developed to: aid in the sampling design; evaluate the remedial approach; and give early indications of future concentrations at compliance locations. However, there were inconsistencies between this model and the conceptual model used for the site. For example, the computed ground water travel times were not consistent with the contamination levels in the downstream wells, and the measured K-2 was not consistent with hydraulic head patterns. Because of these inconsistencies, further study was conducted at the east side of the site to calculate more reasonable travel times and prove that biodegradation was occurring in some areas.

Arnett made the following conclusion: use of the linked, semi-analytical model has been very helpful in identifying data gaps and resolving inconsistencies in the conceptual model. It has provided a foundation for future modeling of fate and transport.

A Comprehensive Simulation Study of VOC Transport in the Vadose Zone and Aquifer at the Subsurface Disposal Area, INEEL: Results and Lessons Learned from the Mother of All Modeling Studies

Jeff Sondrup (INEEL, Lockheed Martin Idaho Technologies Company) opened his discussion on VOC transport by noting that an estimated 88,000 gallons of VOC sludge (CCl_4, TCE, PCE, TCA) from the Rocky Flats DOE facility were disposed of at the subsurface disposal area at INEEL. Vadose zone sampling revealed a plume over a mile wide with concentrations of up to 500 ppm. Ground water concentrations are nondetect to slightly more than MCL. Modeling studies indicated that ground water concentrations will peak at about 125 ppb in 2160. A ROD was signed for the site in 1994, with vapor vacuum extraction as the preferred approach, and five extraction wells began operating in 1996. Ground water concentrations since modeling have been increasing at a much higher rate than that needed to reach concentrations of 125 ppb by 2160. This rapid increase in VOC concentrations has led to the update of the model used at the site.

Sondrup noted that the revised model needed to not only simulate VOC fate and transport, but also be: (1) realistic and representative; (2) conservative where realistic estimates were not available; (3) technically justified for the conceptual model and parameterization; (4) a consensus decision reached by Agency staff. The following assumptions were used to develop the model:

- A flow model was adequate (for both the vadose zone and aquifer)
- Variable infiltration and historic flooding occurs
- Release is controlled by container failure and diffusivity from sludge
- Basalt (the underlying bedrock) acts like a dual-porosity system
- Transport of aqueous and gaseous phases occurs by diffusion and advection
- Equilibrium partitioning is described using linear sorption coefficients and Henry's constants
- Degradation is not included

According to Sondrup, these assumptions were used to develop the model using a three-dimensional lithology that included basalt flows and major sedimentary interbeds. Strengths of the model developed include: (1) All potentially important transport processes are accounted for (excluding degradation); (2) it provides a good match to vadose zone vapor concentrations in the Surface Disposal Area; (3) it accurately predicts ground water data in wells near the Surface Disposal Area; and (4) it points out possible underestimation of the source mass. Unfortunately, the model does not account for VOCs present at outer wells, and has a large computational burden. Overall, creation of a sophisticated, multi-phase, multi-process, deterministic model is possible, but not very practical due to time and resource constraints. In the future, it is recommended that the vadose zone and aquifer portions be separated into different models.

PUMP-AND-TREAT

Pump and Treat Optimization

Kathy Yager (TIO) discussed TIO's current optimization efforts. TIO is looking to compile information on ways that pump-and-treat systems are being optimized, what works and what does not, and whether any systematic approaches are being used. So far, TIO has contacted more than 500 RPMs and State managers to discuss optimization and has received 60 responses. Private industry contacts, consultants, and DOE and DOD personnel have been contacted as well. DuPont was particularly interested and claims that it has optimized between 20 and 25 of its pump-and-treat systems, saving them up to 25% of their costs.

As part of this effort, TIO also has conducted literature reviews to find state-of-the-art practices being used for optimization modeling and alternative optimization strategies, and technologies being used as part of treatment trains with pump-and-treat systems. So far, they have identified four: SVE, surfactants/cosolvents, bioremediation, and treatment walls.

TIO hopes to develop a combined report on this effort, which will include examples of pump-and-treat optimization, a summary of their literature review, and a bibliography of articles. In addition, it hopes to hold a symposium to discuss examples of optimization and to identify priority topics, which may include:

- streamlined long-term monitoring
- mechanical adjustments
- pulse pumping
- computer/remote control
- optimization modeling
- system enhancements

TIO hopes to sponsor a Hydraulic Optimization Simulation Project, otherwise known as "The Demonstration." This will be conducted with TIO, the TSP, and HSI GeoTrans. The objectives of this project will include:

- evaluate existing pump-and-treat systems
- hydraulic optimization modeling
- improve performance or reduce cost
- before and after picture (costs/efficiency)
- off-the-shelf technology
- public domain (MODMAN-LINDO)
- increase awareness
- encourage adoption of technology

As part of this effort, TIO plans to identify 4-7 sites for demonstration in partnership with DOD, DOE, Superfund, Private Industry, RCRA, and state agencies. The following selection criteria will be used to identify these sites:

- system operation > two years
- simple geology/hydrogeology
- no fractured bedrock
- pumping from no more than two aquifers
- adequate ground water flow model (MODFLOW)
- model five layers or less
- modeling report
- demonstrated need
- willingness to implement results

The expected outcome of the Demonstration Project is performance modification, including adjustments to pumping rates, installation of new wells, elimination of existing wells, and development of a cost-benefit methodology. This methodology will ask the following questions:

- Is the current system operating as designed?
- What drives the remediation costs?
- Is the objective containment or cleanup?
- What is the importance of mass removal/time?
- What is the significance capital versus annual expenses?
- Are new technologies available for plume?
- What is the change in plume extent since design?
- Was re-injection applied?
- Were separate treatment trains used?

A Project Review Panel, consisting of experts from academia, EPA, DOD, DOE, consultants, and industry will be formed. After the project is completed, an effort to validate the project data will be made. This will include selection of individual sites, implementation of proposed modifications, and performance documentation.

The schedule for the project is as follows:

- February: Site Selection
- April: Mid-Project Review Meeting
- June: Simulation Completion
- July: Draft report, “end-of-project” meeting, and peer review
- September: Final Report

Sites that are being considered for the Demonstration Project include DOE’s Lawrence Livermore National Laboratory and the Savannah River Site; and five Superfund sites [Bayou Bonfouca (R6), Bofors-Nobel (R5), Kysor (R5), BF Goodrich (R4), and Goose Farm (R2)]. No DOD sites and private industry sites have been proposed at this time.

Cost Performance Data From Ground-Water Pump-and-Treat Actions

Linda Fiedler (TIO) discussed a new database being developed by TIO. The database is being developed with contractor help from TetraTech, Inc., and ERG, Inc., who are responsible for collecting detailed information on ground-water remediation case studies. Thus far, most of the case studies involve pump and treat; however, some *in situ* treatments are included. Fiedler said that the purpose of compiling the data is to evaluate the performance and cost of remediation.

The criteria for selecting sites for inclusion in the database include: 1) long operating periods of the treatment systems; 2) sites having ground-water clean-up goals (not just containment goals); and 3) available cost and performance data. Seventeen pump-and-treat sites have been selected from across the U.S. The systems have been operating for at least 2.5 years. The primary contaminants being treated are chlorinated VOCs, but other treated contaminants include BTEX, PCBs, other SVOCs, and inorganics. Fiedler noted that the database currently lacks information on the presence of NAPLs. She added that the database contains information on plume size, site conditions that increase the complexity of a site (*e.g.*, the presence of more than one contaminated aquifers), system design and operation, effluent discharge, system optimization, treatment goals, system performance, and cost.

Questions and Answers

Mark Ferrey (Minnesota Pollution Control Agency) asked why only 17 sites have been included in the database. Fiedler explained that a detailed evaluation of ground-water remediation is being conducted, and there is a tradeoff between compiling lots of data for a few sites and little data for many sites. Another participant asked whether all pump-and-treat systems are used solely for treatment, or whether they also are used for containment. Fiedler said that containment may have been a secondary goal of some of the systems.

RISK ASSESSMENT

An INEEL-Wide Ecological Risk Assessment Approach

Walt Sullivan (INEEL) indicated that less than one percent of the 890 mi^2 INEEL is industrialized. The industrial facilities are small in comparison to the surrounding natural areas. Most of the INEEL property is a sagebrush/steppe environment. Sullivan commented that the flora and fauna do not recognize property boundaries and can be found throughout INEEL. The dominant flora species include juniper woodlands, sagebrush, rabbit brush, salt desert scrub, and grasses. The dominant fauna species include coyotes, bobcats, mule deer, snakes, and insects. In addition to these species, there are numerous sensitive species, including peregrine falcons, bald eagles, and the northern sagebrush lizard.

The INEEL is a CERCLA site and is being operated under a Federal Facility Agreement/Consent Order. There are several waste area groups (WAGs), each of which is undergoing a comprehensive analysis. Stakeholders are involved in the process via a Citizens Advisory Board.

A comprehensive analysis has been completed for each of the 10 waste area groups (WAGs) at INEEL. WAG-10 includes all of the INEEL property not covered by WAGs 1-9. The objectives of the ecological risk assessment (ERA) at WAG-10 and the other WAGs are to:

- define the extent of contamination from each WAG;
- determine potential effects on populations and sensitive species;
- provide information for developing remediation criteria; and
- establish a baseline for subsequent ecological monitoring.

A hypothetical conceptual model has been developed for INEEL, and the food web is being studied. Ecological sampling was conducted within a three mi^2 sampling area at INEEL during the summer of 1997.

Sullivan said that the controversial nature of ERAs poses interesting challenges. Site characterization is commonly difficult, primarily due to the lack of data. It is also difficult to find laboratories that provide the required analyses. Furthermore, the value of ERAs is considered small when compared to human health issues and the overall cost of cleanup. Sullivan acknowledged that there are certain inherent uncertainties in performing ERAs, but he believes they can be improved. He noted that another important challenge with ERAs is resolving the disagreement by Native Americans as to important issues.

In conclusion, Sullivan noted that consensus science is a challenge, and it is difficult to balance science and budget. Uncertainties in ERAs are often omitted or ignored.

Questions and Answers

Paul Leonard (Region 3) asked whether there are any results of the ERAs. Sullivan indicated that results have been compiled at the WAG level and that contaminants have been detected, but their effects have not yet been proven. Contaminants with a potential effect on the ecology so far have been determined to be mercury, lead, chromium, strontium, and cesium.

Sullivan asked that future questions be directed to:

Robin Van Horn
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VOC REMEDIATION

Investigation into the Influence of Air Rotary Drilling On VOC Concentrations in Sediment and Soil Gas

Jim Studer (Los Alamos/Sandia) opened his presentation by noting that bias and error are typically associated with subsurface investigations. Drilling methods may be the source of bias and error later subsequent soil or soil gas sampling at the borehole. Air rotary drilling forces air down the drill string to the bit. The air cools the bit, keeps the borehole open, and forces drill cuttings to the surface. Air rotary drilling can introduce error and bias into samples by volatilizing VOC contamination. An air rotary causing hammer (ARCH) method was used to study this problem.

The ARCH method hammers the casing 2-5 feet ahead of the bit. Large air compressors exert 1,400 standard cubic feet per minute (scfm) pressure into the ground. ARCH is suspected to impact VOC distribution by displacing VOC-laden soil gas as the air is injected. In addition, it is suspected that VOCs and pore water are stripped from the surface of soil particles. Complex circulation patterns created during drilling may cause mixing and dilution of VOCs.

The impact of ARCH drilling was studied at Sandia at a site historically used for chemical waste disposal. Concentrations over 1,000 ppm VOCs have been detected in the vadose zone. The ground-water table is located approximately 500 feet below ground surface and contains alluvial and colluvial deposits.

In situ tubing placed outside the existing well casings were used as control points to sample soil gas while drilling nearby ARCH wells. There were sufficient sampling points to obtain soil gas concentrations at several wells before, during, and after drilling. Use of Simulprobe® to sample the drilled hole enabled the collection of soil and soil gas samples at the same depth. The Simulprobe® was advanced as far ahead of the bit as possible. Before recording photoionization organic vapor analyzer (PID/OVA) readings, the probe was purged. Samples were retrieved using a wireline tool (although a vacuum can be applied to collect samples) and analyzed for toxic organic compounds. Baseline samples were collected 30 and 90 days after drilling and construction of the sampling ports. Two rounds of samples were also collected at the start-up of the soil vapor extraction (about 60 days and 90 days later).

Comparison of the PID/OVA readings and the results of EPA Method TO-14 analyses showed good correlation of data (R^2= 0.922). The concentration of VOCs were observed to increase significantly from drilling to baseline then decreased during start-up; however, there were some counter trends. One of the major factors affecting these trends was the distance between the Simulprobe® and the drill bit, which was never greater than 4.5 feet in length. When the distance was greatest, the drilling PID/OVA readings were higher than the baseline readings.

In conclusion, the Simulprobe® sampler and the *in situ* port design were effective in documenting the effect of ARCH drilling on soil gas concentrations. The ARCH method was found to cause an artificial depression of the VOC concentrations in soil gas during drilling. This effect can be significant and must be considered when drilling with air rotary. Factors contributing to this effect are the depth of Simulprobe® penetration, contaminant characteristics, drill rig characteristics, and geology. An alternative may be to use dual-tube percussion drilling methods, but some air may still escape into the borehole at the bottom of the casing.

Questions and Answers

Bill Brandon (Region 1) asked whether the same effect is anticipated below the water table. Studer replied that it was. Evidence of this occurred at another site where drilling of a borehole caused the cap of a monitoring well 30 feet away to blow off. Dick Willey (Region 1) asked how long it took to get a representative ground-water sample from the well. Studer indicated that he was not examining this issue at the site, but he waited 60 days before collecting the sample. Future work could involve comparison of samples collected at earlier intervals.

PERCHLORATE

Detection of Perchlorate in Water Supplies

Joe Donnelly (Lockheed Martin) discussed methods recently developed to detect perchlorate in water at low enough concentrations for environmental applications. He provided the following abstract of his presentation:

Perchlorate anions have been found in water supplies and in drinking water. Potential sources for this contaminant in the environment include synthesis and research activities, solid rocket fuel usage, refurbishing and cleaning and use in rocket motors, munitions, fireworks, matches, cattle feed, and medicines.

The California Department of Health Services (DHS) has developed an interim analytical method protocol for the detection of perchlorate to address interim health guidelines. The method detection limit of 0.7 ppb in reagent water addresses the desired 4 ppb detection limit in aqueous environmental matrices, and an 18 ppb action level. This ion chromatographic (IC) method has been used to detect perchlorate in groundwater and surface water supplies in California, Arizona, and Nevada.

Goals for an analytical method include that it be simple, rugged, use widely-available equipment and expertise, be cost-effective, reliable, and produce data of known and adequate quality. These goals must be achieved and documented to support risk assessment activities.

The California DHS method (published 6/97) is based upon ion chromatography, using a strong base eluent. Strong acid is used to regenerate the Dionex AG5/AS5 column pair after analysis.

The column pair (guard and analytical) is a resin-based anion-exchange type, from which perchlorate elutes relatively late (about 7.5 minutes retention time). A general conductivity detector is used. The method detection limit is 0.7 ppb in reagent water, and the reporting limit is 4 ppb. The Cal-DHS has conducted routine monitoring with their method for some months. Dionex has developed a related method using their AG11/AS11columns without the p-cyanophenol deactivator that is used with AG5/AS5 columns.

Both Alltech and Waters are developing methods using carbonate eluents and silica-based IC columns. Alltech has reported detection of 5 ppb perchlorate at a good signal to noise ratio with their system. This result is potentially significant both as an alternative primary analytical procedure, and as a second-column confirmation of perchlorate identity and quantity. The potential for false positives and false negatives should be studied. Potential analytical interferences could include iodide, bromate, iodate, thiocyanate, sulfate, and nitrate anions. The ion chromatographic retention time of perchlorate shifts with concentration. For example, one research group reported a retention time of 35 minutes for a 50 ppm solution. This time was shortened to 20 minutes for a two parts-per-thousand solution. Confirmatory analytical techniques would be desirable, both qualitative (identity) and quantitative (precision and accuracy).

Other methods for perchlorate analysis are available, but either are not suitable or have not been optimized for trace-level environmental analysis. Capillary electrophoresis has been applied to perchlorate analysis in the ppm concentration level with general detectors, such as ultraviolet, and with specific detectors, such as Raman or mass spectrometric. Electrospray mass spectrometry has also been used to detect perchlorates.

The capabilities of the IC type of method should be defined, with respect to the confirmation of analyte identity and absence of interferences (false positives, false negatives). Single and multiple laboratory precision and accuracy, sample holding times, and sample preservation should be investigated. Matrix effects such as dissolved solids/conductivity should be determined.

One goal for future research is to determine the stability of perchlorate in the environment, particularly in aqueous ecosystems. The thermodynamics of perchlorate decomposition are favorable. Thus, it is potentially a powerful oxidizer. The kinetics are slow at ambient temperatures and in the absence of catalysis. Certain biological systems are known to provide biochemical degradation pathways that are kinetically favorable. Bioremediation of perchlorate has been applied with some success. The relative toxicity of the perchlorate anion in drinking water will depend therefore upon risk assessment and upon its persistence in biologically active water supplies.

In summary, the following laboratory-based studies of the Cal-DHS method are being considered:

- detection limit validation in aqueous matrices;
- verification of method performance with high dissolved solids;
- method precision, intra- and inter-laboratory;
- method accuracy vs. confirmatory analysis results; and
- sample stability and preservation study in various source waters vs. holding times.

Questions and Answers

In response to a question from Harry Craig (Region 10), Donnelly indicated that there is a good chance of finding ammonium perchlorate at a site with the recent improvements in the detection limits of analytical methods. He indicated that thousands of tons of waste must have been buried in Henderson, Nevada, to result in the 1 ppb perchlorate detected in Lake Mead.

Jon Josephs (STLP for Region 2) asked where project managers should have their samples analyzed if they suspect that perchlorate is present at a site. Donnelly indicated that the choice of laboratories depends on whether or not the sampled water is similar to the water used as the standard for the particular laboratory's method. If it is not similar to any of the standards, the project manager should contact Ken Brown at NERL-Las Vegas. Donnelly confirmed that false positives, rather than false negatives, are more likely at commercial laboratories. He noted that laboratories in states other than California are also performing the DHS method.

In response to another question, Donnelly indicated that different remediation methods, including bioremediation, have been examined for perchlorate, but they are expensive. There is currently no off-the-shelf technology available. Stopping migration of perchlorate at the source may be one alternative.

SITE CHARACTERIZATION

Lead Soil Contamination Investigation Using XRF Field Screening and GPS Techniques

Skip Wrightson (IT Corporation) discussed an investigation that was conducted at a site at Sandia National Laboratories, New Mexico. There are two intersecting trenches at the 20-acre site. During the Cold War, Sandia tested nose cone impacts at this location. Barrels made of lead were blown up, scattering lead particles of various sizes across the site. Geoprobe sampling and analysis of boreholes confirmed that most of the contamination was in the upper few inches of the soil profile. An industrial clean-up level of 2,000 ppm lead was negotiated for the site.

The purpose of the investigation was to use a single-phase approach to characterizing lead contamination in soil and removing the contaminated soil. A statistician predicted where the highest lead concentrations would be, based on the results of Geoprobe soil sampling, then a sampling grid (on 30-foot intervals) was set up over the site using the Global Positioning System (GPS).

Soil samples were collected at the grid nodes and analyzed using field x-ray diffraction (XRF). Over 600 XRF analyses were run in the field over a period of approximately three weeks. Each sample took 7-8 minutes to run. The laboratory trailer was equipped with a fume hood and HEPA filters. The XRF unit's calibration was tested every 10 samples, but the calibration did not have to be adjusted often. The calibration standards were prepared with local soils spiked with lead and analyzed using ICP.

Areas with soil exceeding lead action levels were excavated and then resampled. If soil lead concentrations still exceeded action levels, additional soil was excavated. A total of 300 cubic yards of contaminated soil was excavated and disposed. Confirmatory sampling to assure that the lead had been removed was conducted using indirect current plasma (ICP) analysis (EPA Method 6010).

The total cost of the investigation was $367K, which included $167K in disposal costs ($550/yard). This cost is low compared to the projected cost of $1.03M that would have been required for the investigation if statistical grid sampling and field analyses were not conducted. As a result, the portable XRF unit appears to be a cost-effective technology for cleaning up lead contaminated soil.

The single-phase approach minimized the downtime for field crew and equipment, unit costs for analyses, and investigation-derived waste. The approach also allowed flexibility to make field decisions as site conditions changed. The limitation of the approach was the inconsistent correlation of the XRF data with the ICP data due to the nugget effect. Minimizing this effect would require pulverizing the soil samples to remove large nuggets. It was recommended that correlation factors or sample preparation techniques be determined before starting future investigations.

Development and Use of Environmental Geophysical Technologies at the INEEL

M. Cathy Pfeifer discussed the development and use of environmental geophysical technologies at the INEEL. Below is her written abstract of her presentation:

Multiple characterization techniques are used at the INEEL because, like most other sites where remediation options are being considered, the problems encountered at the INEEL are complex in nature and cannot be effectively characterized using only one technique. Using a suite of non-intrusive and intrusive characterization techniques can provide complimentary information on multiple parameters to better understand the subsurface conditions at a site. Thus, at the INEEL emphasis has been placed on the development of a suite of tools to characterize a site to provide investigators with more flexibility in designing the remediation characterization activities. To effectively develop and deploy these characterization techniques to remediation activities, the long-term goal of the remediation activity needs to be considered. For example, characterization for large-scale retrieval has a different goal and set of needs than does characterization for long-term *in situ* stabilization. For large-scale retrieval activities, using multiple characterization techniques provides investigators with better waste volume estimates and also more information on the types of waste present than is possible using only one technique. In designing long-term stabilization activities, utilizing a variety of characterization techniques provides the investigator with a more complete image of the subsurface from which to begin verification and monitoring activities.

At the INEEL several geophysical systems have been utilized, modified and developed to provide the optimal information for characterization, for remediation planning and execution. These activities include, the development of the Rapid Geophysical Surveyor (RGS), participation in the development of the broad band Very Early Time Electromagnetic (VETEM) system, the demonstration and use of emerging technologies, and the integration of standard geophysical systems for improved subsurface characterization. The RGS is a magnetometer system capable of collecting data at a high rate of speed with high spatial fidelity. The VETEM system is being developed by a consortium of national laboratories and universities to integrate data acquisition and high resolution data imaging for a suite of electromagnetic methods including a new system operating in the bandwidth between traditional induction electromagnetics and radar systems. During the VETEM project, a demonstration of state of the art electromagnetic systems available for use was performed at the INEEL to collect a large data set to develop and test improved interpretation software being developed by the VETEM team. Other environmental characterization activities performed by INEEL personnel have included detection of waste sites such as pits and trenches at the INEEL and other sites.

Dye Tracer Study to Determine the Potential for Contaminant Migration in Ground Water and Source Determination for PAH Contamination

Bill Brumley (NERL-Las Vegas) explained that this study was conducted to determine whether tracer dyes injected at one site could migrate to an adjacent sites. He noted that tracer dyes are absorbed by charcoal pads placed at the bottom of wells, and detected by spectrofluorescence. Using capillary electrophoresis, the detection limits of fluorescein and tinopal have been shown to be significantly reduced, to 22 ppt and 88 ppt, respectively. Petroleum-based carrier fuels and coal-derived materials (creosote) show distinct apportionment patterns in a given formation. Saturates are relatively high in crude content and low in coal. Capillary electrophoresis demonstrates that basic cations migrate under low pH conditions. Therefore, outlining source apportionment depends on finding unique methods of measurement.

Questions and Answers

Brumley was asked if natural attenuation affects source determination. Brumley replied that weathering is a factor, but it is not currently accounted for in this study.

Consortium for Site Characterization Technology

Eric Koglin (NERL-Las Vegas) explained that the goal of the Environmental Technology Verification Program (ETV) is to promote the acceptance and use of innovative environmental technologies. This is accomplished by providing credible performance data to purchasers and permitters of environmental technologies. Within ETV, the Consortium for Site Characterization Technology (CSCT) facilitates the demonstration, evaluation, verification, and use of innovative monitoring, measurement, and site characterization technologies.

CSCT clients include technology developers, users, and regulators. CSCT activities begin with identifying the needs of the user community. Then technology availability is determined. Next, qualifying vendors submit simple proposals to address user needs. These proposals are evaluated by CSCT and qualified vendors are invited to participate. Test plans are developed in accordance with guidance by the vendors and the verification organization. Field testing is then performed at two sites. A verification report and verification statement is then prepared and reviewed. Finally, dissemination and outreach for the verified technology is performed.

CSCT has active partnerships with Sandia National Laboratory and Oak Ridge National Laboratory. Two sets of verification reports already have been completed, in addition to a *Guidance on Demonstration Plan Preparation*. Four more verification report sets are in progress, and plans are in place to solicit technologies in FY98 and FY99.

CSCT supports field analytical technologies through: (1) promoting acceptance at the national and state level; (2) Vendor FACTS, a Windows-based database that provides vendors' information on field portable technologies for measuring and monitoring contaminated soil and groundwater at sites; (3) the Navy/EPA Field Sampling and Analysis Technologies Matrix and Reference Guide, a joint Navy/EPA document patterned after the Remediation Technology Matrix; (4) ETV and CLU-IN Web pages; and (5) exhibits at conferences and trade shows.

Questions and Answers

Koglin was questioned about decision support tools as a topic for the FY99 Technology Solicitation. Koglin elaborated, stating that it would include sampling network design software and data assessment tools. However, Koglin stressed that they are not sure how they are going to evaluate those technologies at this point.

The Partitioning Interwell Tracer Test at a Chemical Waste Landfill

Jim Studer (Los Alamos/Sandia) explained that sites characterized with NAPLs are highly problematic due to the challenges of characterization and remediation. NAPL is often difficult to detect in the subsurface, no options have been available for quantitative evaluation, and no improvements in remediation can be expected without accurate characterization. The Partitioning Interwell Tracer Test (PITT) locates subsurface NAPL pools, lenses, and residuals in the unsaturated or saturated zones, provides a quantitative estimate of NAPL saturation within the test zone, and has the ability to sample a large volume within an aquifer. With these capabilities, the PITT can be used for site characterization, as well as assessment of NAPL remediation systems. The system operates by injecting a set of tracers into an injection well. Some of these tracers must sorb with NAPL, and others must pass through unaffected. Then a chromatographic separation is created to estimate the quantity of NAPL present.

Studer noted that the PITT system was field tested at the Chemical Waste Landfill at Sandia National Laboratory, where solvents were disposed of more than 30 years ago. The landfill is contaminated with solvents at depths up to 12 feet, and record keeping for the site indicates that between 1,000 and 10,000 gallons of NAPL were disposed at the site. Two injection wells were drilled 55 feet apart and screened from 20 to 80 feet in three separate zones to better observe any vertical stratification that might be present. Within the shallow zone, the average TCE saturation was estimated to be 0.15%. The intermediate and deep zones showed no residual TCE contamination. Since the initial PITT, voluntary corrective action has taken place, and the amount of contaminant removed correlates well with the amount estimated to be present using PITT. According to Studer, this supports the conclusion that PITT is the only technology currently available that can be used to quantify the three-dimensional nature of NAPL over a representative volume of the vadose or saturated zone.

Questions and Answers

Kay Wischkaemper (Region 4) asked for an estimate of how much it would cost to perform a PITT. Studer replied that it cost approximately $2 to $3 per gallon of swept pore volume. This cost incorporates the entire process, but only applies to larger scale projects.

Studer was asked how PITT would detect TCE that had settled into a clay lens depression. Studer replied that by using continuous core data, the pool could be accounted for if the tracer were able to intersect the upper surface of the pool. A participant followed by asking what would happen to the results if continuous core data were not available. Studer replied that the results would not be able to incorporate the pooled TCE.

On-Site Analysis of Soils Contaminated with Explosives Using Ion Mobility Spectrometry

Alan B. Crockett (INEEL) explained that there are approximately 200 explosives-contaminated sites in the U.S. and 1.6M yd^3 of contaminated soil. These explosives are often heterogeneously distributed and therefore require high density sampling. Because of these costs, development of on-site analysis methods is essential to performing site characterization more quickly, economically, and accurately.

According to Crockett, past analysis tools included colorimetric and immunoassay methods available include EnSys, D-Tech, and ENVIROL. However, these methods are expensive and have limited throughput. In contrast, Ion Mobility Spectrometry (IMS) has been in use for several years to detect explosives in air, but its application to soil detection has been limited.

Crockett noted that IMS can quantify the presence of multiple explosives simultaneously at a material cost of about one dollar per sample. The data produced by IMS are suitable for use in risk assessment. Current technology limits IMS to the quantitative detection of a contaminant only if it is the sole contaminant in the sample, because of competitive interference among the explosives and the solvent. However, a qualitative detection of several contaminants can be made using a single sample. In addition, IMS is not yet a proven technology.

Crockett said that in the future, a suitable GC/IMS software program needs to be developed for both the identification and quantification of compounds. A GC column also will be incorporated into existing equipment to separate analytes and reduce solvent content. A split injection port will be added to facilitate dilution. Once these improvements are complete, the system will be used to test a suite of well-characterized soils. Then a field test will be conducted at INEEL, followed by a demonstration for SERDP, ESTCP, or EPA.

INEEL plans to work with manufacturers to develop an instrument that can perform IMS. This instrument must have a GC column, split injection port, system software for identification and quantification, a GC bypass injection port for screening, and the ability to verify the presence of mines and UXO. The manufacturer will benefit by obtaining exposure, sales, and recognition for the product. FemtoScan is interested in pursuing the project.

According to Crockett, the use of IMS for detecting explosives in soil shows promise, but its effectiveness remains to be demonstrated in the field. It has the ability to screen for multiple explosive compounds simultaneously, with a future potential for quantitative results. This technique also may be suitable for water analysis using solid phase microextraction. The ultimate goal of this project is to provide adequate validation to EPA for inclusion of the method as an on-site procedure in SW-846.

Questions and Answers

Crockett was questioned on the form of output the instrument would produce. Crockett replied that the instrument will port directly to a workstation, and that the software for analyzing the samples is under development.

SAMPLING

New Standard Sampling Procedures for Sampling Soil Contaminated with Volatile Organic Compounds

Alan B. Crockett (INEEL) explained that VOCs in soil exist in different phases, including vapor, dissolved in aqueous, liquid, and sorbed to solid phase. The old EPA method for measuring these VOCs (EPA SW-846 Preparation Method 5030A) consisted of filling a bottle with soil with no headspace, preserving the sample by chilling to 4°C, opening the jar and stirring the sample, rapidly weighing out 5g of soil, adding purging solutions, purging the VOCs from the sample onto a Tenax trap, thermally desorbing the VOCs onto a GC column, and then analyzing the sample. This method led to significant VOC loss during field sampling, transit and storage, and subsampling.

The old ASTM method (D4547-91) offered several advantages over EPA SW-846: core sampling, VOA vials with special adapter caps, field methanol immersion, and composite sampling into methanol. However, this ASTM method had some disadvantages: it permitted use of a core metal core cylinder with end caps and bulk sampling into non-airtight bottles.

Use of both the old EPA and ASTM methods led to reported results that were 10 to 1,000 times lower at day zero, with additional losses for some compounds at 14 days. Because of this, an improved sampling procedure (draft ASTM D4547) is being prepared by the ASTM/EPA Accelerated Standard Group. Significant changes reflected in this new procedure include:

- preparation of a fresh surface before sampling and handling
- flexible backed PTFE caps for containers
- use of a coring device for sampling
- a requirement for containers containing samples with no methanol to remain closed at all times
- collection of field composite samples in methanol
- use of a special coring device (EnCore™) for sampling and 48-hour storage
- a recommendation against the use of metal core rings and end caps
- a recommendation that a preservative be added to all samples

Two new EPA methods also are being developed: EPA SW-846 Method 5035 and EPA SW-846 Method 5021. EPA SW-846 Method 5035 is a closed system purge-and-trap method in which a 5-g core is collected using a special vial that is never opened. This method permits field sampling into sodium bisulfate (a preservative), sample freezing for alkaline samples, and sample storage in an EnCore™ sampler for 48 hours. Sampling into methanol may be considered for high concentration samples. Bulk soil sampling without sample preservation is permitted, but only if septum caps are used. Method 5035 is limited by: a single analysis per sample, so multiple samples are needed, applicability to a limited concentration range, effervescence on carbonaceous soils, analytical bias on some samples due to incomplete extraction, lack of composite sampling into methanol, and shorter holding times for unpreserved low level samples.

EPA SW-846 Method 5021 samples VOCs in solids using headspace equilibrium by placing a 2-g soil core into a septum cap vial; preserving the sample in the field by adding NaCl and lowering the pH to 2; and opening of the vial for the addition of a matrix-modifying solution. Limitations of Method 5021 include a loss of VOCs when the vial is opened to add the matrix-modifying solution in the laboratory; puncture of the septum when sampling into the matrix-modifying solution, potentially losing VOCs; holding times are not extended for preserved samples nor shortened for unpreserved samples; field operation is more complicated; and only one analysis per sample is permitted.

In summary, Crockett noted that the new ASTM standard is more complete in preanalytical sample handling, provides more guidance on sampling options, extends holding times, and permits collection of more representative composite samples. The new EPA methods reduce VOC losses compared to previous methods, improve sample preservation, and are biased against the field methanol method. The differing results obtained for the same sample from different analytical methods pose difficult questions for remediation criterion decisions.

Questions and Answers

Izraeli asked Crockett if ASTM and EPA were working together on the development of new procedures. Crockett replied that EPA is just funding and supporting ASTM work.

Crockett was asked whether he thought new sampling procedures would have a large effect on distribution coefficients. Crockett replied that they would, adding that he was uncertain which method would be best for remediation characterization.

Another question addressed the qualification used for deciding whether soils can be sub-cored. Crockett answered that the ASTM method bases this decision on whether the soil is cohesive or non-cohesive.

***In Situ* Groundwater Sampler for Volatile Organic Compounds**

Scott Barrie (INEEL) noted that typical ground water monitoring involves purging three well volumes, containerizing purged water, shipping samples for laboratory analysis (with a 45- to 60-day turnaround), and treating the sample and purge water. This leads to high laboratory analysis costs as well as the potential for fines from purge and sample disposal. To address these problems, the *In-Situ* Sampler (ISS) was developed jointly by Lockheed Martin Idaho Technologies Company (LMITCO) and TSI, Inc. This sampler provides information on the vertical distribution of VOCs in ground water and uses semi-permeable tubing to absorb VOCs from the ground water. It can be lowered by hand into a well to various depths to obtain information on the vertical variation of up to five compounds at different contaminant concentrations.

According to Barrie, ISS permits depth profiling of contaminants, quantitative analysis for TCE, and field screening for various VOC contaminants. It simplifies waste disposal, produces quick results, and is very inexpensive. These advantages could be utilized for the mapping of three-dimensional contaminant plumes, identifying the pathway of contaminants traveling through fractured rock, monitoring around underground storage tanks, and locating NAPLs.

Barrie noted that refinements of the ISS system will target increased information on the equilibration times necessary and their dependence on temperature, production of quantitative results for other VOCs, and comparisons against conventional methods.

Questions and Answers

Barrie was asked if the semi-permeable tubing was reused for sampling. He replied that if the tubing is allowed to stand for 24 hours, it degases.

In response to a question about tubing length, Barrie noted that the tubing used is three feet long; longer lengths permit greater precision at lower VOC concentrations.

The issue of vertical water flow in the well was raised. Barrie replied that if there was vertical water flow in the well, each zone would have up to be packed individually, but this was not a problem at the INEEL test site.

Advantages of Composite Sampling in Environmental Sampling

Alan B. Crockett (INEEL) explained that composite sampling offers several advantages over conventional methods: improvement in sampling precision, efficiency in locating hot spots, and reductions in cost due to grater precision. Other benefits include: increased normality of data, greater spatial coverage, anonymity where population rather than individual statistics are needed, and the option to use a single composite for decisions.

Crockett noted that compositing is equivalent to physical averaging, where the precision of a composite is dependent on the number of aliquots in the composite. If sampling error is greater than analytical error and analytical costs are high compared to sampling costs, then precision can be maximized by collecting a composite sample and costs can be reduced by more than 50%. Composite sampling also may be useful in detecting hot spots within a contaminated area. Design of a composite plot is dependent on both the knowledge of contamination present and distribution of contamination at a particular site.

Problems with subsampling include: (1) little care is typically used in subsampling; (2) field method obstacles, such as difficult matrices and the accounting of large, under-represented objects; (3) laboratory subsampling problems, such as the lack of mixing before subsampling, the loss of VOCs during subsampling, and small sample sizes. Many of these issues can be resolved with the upward adjustment of sample sizes and the collection of representative subsamples.

Compositing can be a powerful tool for increasing precision, reducing costs, or both. It is useful for determining mean contaminant levels and finding hot spots. However, it must be applied properly in order to realize these benefits.

Questions and Answers

Crockett was asked about his reluctance to test for VOCs using composite sampling. Crockett replied that composite sampling should not be used to test for VOCs because of the need to assure that samples are representative, which often implies that some degree of mixing must be done.

Crockett was asked if composite sampling could be used to characterize the physical properties of a soil in addition to its chemical properties or contaminants. Crockett replied that if the scale was large enough, and the desired resolution low enough, physical properties of soils could be examined using composite sampling.

One participant argued that compositing by a laboratory could negate the cost savings of composite sampling. Crockett agreed, suggesting that compositing should preferably be done in the field.

Crockett was questioned about the inclusion of large, under-represented objects. He stated that larger grains need to be ground down to have a diameter less than 2 mm and included if the sample is to be truly representative.

DNAPL REMEDIATION

Surfactant Enhanced Aquifer Remediation for DNAPLs at Neutral Buoyancy

G. Michael Shook (INEEL) discussed Surfactant Enhanced Aquifer Remediation and Neutral Buoyancy (SEAR-NB), which is a new method of DNAPL remediation developed by INEEL. SEAR-NB was developed through theoretical analysis, numerical modeling, and laboratory experimentation. To implement it in the field, laboratory work must be conducted to identify the appropriate chemicals to be used in remediation. Next, a conceptual design must be developed that incorporates well field design, pumping rates, pore volume throughput, and expected effluent concentrations. Third, coring and aquifer testing must be conducted to perform additional core analysis and estimate the permeability distribution. Fourth, a Partitioning Interwell Tracer Test (PITT) must be performed to characterize the amount and distribution of DNAPL present. Finally, the SEAR-NB is designed using results from laboratory work, well tests, and the PITT. Field work at INEEL is slated for the Fall of 1998.

Questions and Answers

Shook was asked if both tracer tests could be performed simultaneously. Shook replied that it could be done, even though they use different sets of chemicals. In addition, Shook was asked if vertical profiling would be included in the tracer tests. Shook replied that vertical profiling might be done, but that the matter needs to be discussed with EPA first.

Shook was questioned about the use of PITTs for performance assessment. Shook answered that the PITTs will be run, but the decision on whether they are adequate for performance assessment will be up to EPA.